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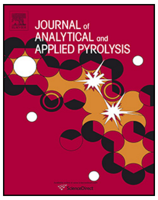

Assessment of sustainable biochar production for carbon abatement from vineyard residues

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ABSTRACT

In the present work ripped vines (*Vitis vinifera*) from the winery industry were pyrolyzed at 550 °C in a pilot plant reactor. Characterization of biomass and pyrolysis co-products was carried out. Mass and energy balances were determined in order to find out whether or not a self-sustainable process was achievable for this biomass by burning the gas and liquid co-products. The energy content in these co-products was 5.52 $\mathrm{MJ/kg_{feedstock}}$ and the surplus energy after meeting the energy demand for the process was about 2.73 $\mathrm{MJ/kg_{feedstock}}$. A mobile and self-sustainable demonstration scale pyrolysis reactor was designed and manufactured based on the findings of the experimentation in the pilot plant reactor. The mobile reactor is self-sustainable, with capacity up to 60 kg/h of ripped vines' wood with little pre-treatment, reaches high working temperatures (up to 800 °C) and has a biochar yield between 25 and 35% depending on pyrolysis conditions. The produced biochar in the mobile pyrolyzer meets the heavy metals content for the class B and C in Spanish legislation on fertilizers and those of the International Biochar Initiative for international and European limits. Using the mobile reactor to produce biochar and applying it at the biomass source (avoiding the biomass and biochar transportation) could lead to a carbon footprint reduction of ≈18 g of CO_{2eq} per bottle of wine or 125.4 tCO_{2eq}/yr.

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1. Introduction

Biochar is the charred solid product from pyrolysis of organic matter, similar to charcoal but intended for agricultural and/or environmental applications. The characteristics of biochar are highly dependent on the type of feedstock and pyrolysis conditions, with temperature being one of the most significant [1–4]. Nowadays, the scientific interest in such material and the mechanisms of its beneficial action in soil is growing [5–7]. Several benefits from biochar application to soil as an amendment are claimed, some of them are: improvement of soil fertility [8–10], neutralization of acidic soils [8], higher nutrient availability for plants [11], and a rise in water holding capacity [12,13]. But also the carbon structures present in the biochar are highly resilient to the soil biological activity. Therefore the biochar might act as carbon storage for long periods of time contributing to climate change mitigation [14].

There are several technologies for charcoal/biochar production [4,15], embracing a wide range of technologies, from old and polluting methods such as mound kilns (without volatiles or liquid recovery not suitable for sustainable biochar production) to modern and cleaner technologies. The latter also enable the recovery of co-products (gas and bio-oil) improving the economics of biochar production [16]. Technologies for sustainable biochar production should include: improved energy efficiency and reduced pollution emissions; recovery of co-products to improve process economics; control of operating conditions to modify yields; and characteristics of co-products; and feedstock flexibility [16]. Some examples are listed next: the Haloclean Pyrolysis Reactor, from Advanced Biorefinery Inc. (ABRI-Tech), the 50 TPD Pyrolysis system [16], the Pacific Pyrolysis Slow Pyrolysis [17], the 3R Zero Emission Pyrolysis Process [18], Pro-Natura Pyro-6F [19] and the fast rotary hearth technology of the BiGchar from Black is Green [20].

The type of feedstock, its characteristics and source should also comply with certain conditions to be considered as a sustainable raw material for biochar production. These conditions are listed in the European Biochar Certification-Guidelines for a Sustainable Production of Biochar (EBC) [21] including: that it must be ensured

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that all non-organic waste such as plastic, rubber, electronic scrap has been removed; must be free of paint, solvents and other organic or non-organic contaminants; when using primary agricultural products, it must be guaranteed that these were grown in a sustainable manner; feedstock used for the production of biochar must not be transported over distances greater than 80 km with an exception made for pyrolysis additives or special biomasses for use in production tests and the International Biochar Initiative (IBI) [22] suggests some information about the feedstock to report, such as: material composition (feedstock ingredients); specify whether the material was processed or not (virgin). The use of the co-products from biochar production to supply energy to the pyrolysis process seems to be promising, there are several studies on energy requirements for pyrolysis of different feedstock [23,24], and the evaluation of self-sustainable processes in bench scale [25].

The winery industry in Spain is the biggest in the world, with a dedicated area for grape production around 954,020 ha in 2012 [26]. Every year old and low grape production vines are pulled off from the soil and new ones are planted. This activity generates vast amounts of woody residues, which commonly are not treated but burnt. The open burning of the biomass releases greenhouse gases (GHGs) and particulate matter threatening both human and environmental welfare. On the other hand, biochar production from agricultural and forestry wastes such as forest residues, mill residues, field crop residues, or urban wastes has an estimated C sequestration capacity of 0.16 Pg C/yr [27]. The worldwide maximum capacity for storing biochar carbon into agricultural soils (1411 million hectares) is estimated to be about 428 GtC [28].

The present work was focused on the development of an alternative management of vineyards' residues from a Spanish winery and on the reduction of its GHGs emissions through biochar production and its later application to the vineyards. It included the design and fabrication of a mobile and self-sustainable pyrolysis reactor (MSPR) for biochar production at demonstration scale fulfilling the requirements for sustainable biochar production previously mentioned. Firstly, a series of tests were performed in a pilot plant pyrolysis reactor (PPR) at the University of León, (Spain). Secondly, the collected data were used for the design and fabrication of the equipment by Mecanotaf S.A., a Spanish engineering company. The motivations for a self-sustainable and mobile pyrolysis reactor were to reduce CO_2 emissions by less external energy requirements and reduced transportation. Once the self-sustainable reactor was built, it was tested and the carbonised product was characterized to evaluate its use as biochar.

2. Materials and methods

2.1. Materials

The biomass used in this work was ripped vines' wood (RVW) (*Vitis vinifera*) from vineyards property of Miguel Torres S.A. (Barcelona), which is one of the biggest wineries in Spain. The vines in this kind of vineyards have a period of profitable exploitation from 30 to 40 years. The amount of wood residues generated by the removal of old or damaged vines in the vineyards is approximately 15 t/ha yearly (35 wt.% water content). The removed vines are left in the vineyards outskirts for a year, after that time, the water content in the wood is reduced to around 10 wt.%. Due to the limitation of particle size (approximately 30 mm in diameter × 60 mm in length) admitted by the feeding system in the pilot plant reactor, the material was passed through a hammer mill before being fed. The only pre-treatment considered for the ripped vines' wood (RVW) to be treated in the self-sustainable reactor was sieving the material trough a 150 × 150 mm mesh.

2.2. Equipment

2.2.1. Pilot plant pyrolysis reactor (PPR)

A series of 15 trials, for co-products yields energy consumption determination, were performed in a pilot plant pyrolysis reactor (PPR) in the University of León, (Spain) under the same operating conditions, 550 °C and 15 min of solid retention time, no inert carrier gas was used. Three representative samples of gas and liquid co-products from trials 5, 10 and 15 were characterized for the energy balance of this pyrolysis process. For the carbonised solid fraction, 3 representative samples were characterised.

The pilot plant experiments were carried out in a semi-continuous electrically heated reactor in which the material to be treated was fed through a hopper with a system of two valves designed to ensure oxygen-free conditions for each of the partial loads. A schematic of the reactor can be found elsewhere [38]. The char container has a limited capacity (100 L) and it has to cool down before char extraction limiting a continuous operation mode. The average amount of treated feedstock was 28 ± 4.5 kg per test.

The reactor is an auger furnace (1400 mm in length × 290 mm inner diameter) with three electric resistances (2.8 kW each one, model Fibrothal HAS 300/375/115, Kanthal, Hallstahammar, Sweden) independently controlled. Each resistance has two thermocouples that detect the temperature near the wall of the reactor and within the center of the chamber, and an accumulative energy meter (Circutor model CI.1 type MK-63D, Barcelona, Spain) to register individually their energy usage. These features allowed automatic adjustment of the temperature along the reactor. The pyrolysis temperature was set at 550 °C for the three heated zones. The gases produced by the pyrolysis process were fed to combustion by means of a centrifugal extractor fan that produced a working pressure of 1006.25 mbar (absolute) inside the reactor. The gas sampling set up included a condensation system which consists in a bubbler and two U shaped tubes (condensate traps) filled with Raschig rings in an ice bath, and a vacuum pump to overcome the extractor fan pressure. The gas samples were collected in glass ampules. The solid co-product was collected in a container at the end of the auger, once cooled. The condensates (liquid co-product) were collected after the extractor fan.

2.2.2. Mobile and self-sustainable pyrolysis reactor (MSPR)

The MSPR consists in two concentric chambers; the inner is the pyrolysis zone and the outer is the combustion chamber for the gases and vapors released by the biomass treatment. There is not carrier gas involved in this pyrolysis process. The feeding system has been designed to minimize any atmospheric air inlet. The reactor reaches the pyrolysis temperature using propane gas which is stopped 10 min after the feeding begins. The feeding of the material to the pyrolysis chamber starts once the target temperature in the pyrolysis chamber is reached. The feedstock is charged in a conveyor belt, and then it is elevated by a bucket elevator to the feeding auger on top of the pyrolysis chamber. The heat is transmitted to the biomass through the metal walls of the pyrolysis chamber. Then, due to thermal degradation, the material begins to release condensable and non-condensable gases. These gases are conducted through pipes, kept at the pyrolysis temperature, to the combustion chamber without liquid formation. The thermal energy for the pyrolysis is supplied by the combustion of the vapors and gases of the pyrolysis process. It is maintained by the steady stream of pyrolysis gases to the combustion chamber; at this point the MSPR is thermally self-sustainable. As the carbonised product reaches the lower part of the pyrolysis chamber, it is transported by another auger at the bottom to the cooling deposit. The MSPR is shown in Fig. 1. Due to the current patent process of the MSPR, sensitive

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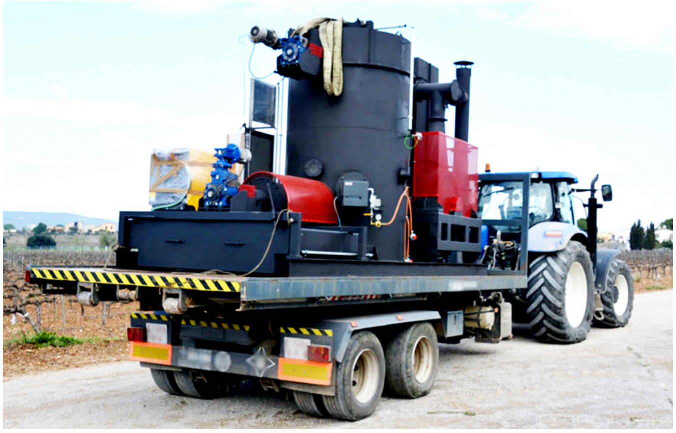

Fig. 1. Photograph of the MSPR being towed by tractor.

information is not given (patent application number: P201431105, Oficina Española de Patentes y Marcas).

2.3. Analysis techniques

2.3.1. Feedstock, ripped vines' wood (RVW) and charred solid products

Proximate analysis was performed to determine total moisture, volatile matter and ashes according to UNE-EN 14774-1:2010, UNE-EN 15148:2010 and UNE-EN 14775-2010, respectively. Carbon, hydrogen and nitrogen content were determined in a LECO CHN-600 analyser following ASTM 5373. The fixed carbon (FC) was calculated by subtracting ash and volatile matter contents from 100% (in a dry basis). Total sulphur content was determined with a LECO SC-132 analyser according to ASTM 4239. Oxygen content was obtained by difference. The heating value was determined with a LECO AC-300 analyser using an adiabatic method in accordance with UNE-EN 14918:2011 (all LECO equipment, LECO Corporation, St. Joseph, Michigan, U.S.A.).

2.3.2. Charred solid product from the mobile and self-sustainable pyrolysis reactor (MSPR)

The charred solid product was firstly characterised following the techniques described in Section 2.3.1, and secondly for the determination of parameters of interest in a biochar such as, pH, electrical conductivity, organic matter, phosphorus, ammoniacal nitrogen, nitric nitrogen, organic nitrogen, carbonates and heavy metals.

The techniques used for the second characterisation are described next.

The pH and EC values were determined in a water extract (1:25 w/v) of the sample, after mechanical stirring for 1 h. The pH measurement was determined in the supernatant with a pH meter GLP22CRISON, and the EC (25 °C) with a conductivity bridge WTW LF330, both previously calibrated.

Organic carbon: determined by the Walkley–Black method. A 125 mg sample was digested in 7 mL of 0.25 N potassium dichromate and 20 mL of sulfuric acid for 120 min at 150 °C. Excess potassium dichromate was assessed on a titrator Metrohm 862Copact Titrosampler.

Organic N: Kjeldahl method, whereby the sample is digested in sulfuric acid in a digester DS-20 Tecator, transforming the N in ammonium sulfate. It is then distilled in a distillation unit Kjeltec System 1030 (Tecator) and finally titrated with boric acid.

Ammoniacal N: extraction in potassium chloride, the extract was filtered and measured with a Metrohm 692 pH meter coupled with a selective ammonium ion meter No 133/1, and a temperature probe.

Nitric N: Nitrates are extracted from the sample with a saturated solution of calcium sulfate and determine by reading in the second derivative UV–vis spectrophotometer DU 640 (Beckman).

Carbonate: determination by the Bernard calcimeter technique at constant pressure and temperature.

Phosphorus: the Olsen–Watanabe method was followed. Phosphorus was extracted from the sample with sodium bicarbonate at an approximately constant pH of 8.5 and then the absorbance of the extract was measured on a spectrophotometer DU 640 (Beckman) for a wavelength of 882 nm.

Calcium, Magnesium, Potassium, Sodium, Iron, Manganese, Copper, Zinc, Boron, Cadmium, Chromium, Mercury, Nickel and Lead by wet digestion, 0.5 g of the sample digested in 10 mL of nitric acid (65%), 3 mL of hydrochloric acid (37%) at atmospheric pressure in a digestion tube with reflux, the digested samples were analyzed by inductively coupled plasma- mass spectroscopy (ICP-MS) reading with a KED cell for interference elimination.

2.3.2.1. Gases.

The identification and quantification of gas species were necessary for the gas heating value determination. Gaseous samples taken in glass ampoules were analysed in an HP 5890 (HP-Agilent, Santa Clara, California, U.S.A.) chromatograph using three separation columns and two detectors. A semi-capillary column HP-AL/S (50 m long × 0.35 mm inner diameter) was used to analyse hydrocarbons (C_xH_y) with helium as the carrier gas and with a flame ionisation detector (FID). A 5 Å molecular exclusion packed column (1.83 m long × 3.175 mm outer diameter) with a mesh size of 60/80 was used for H_2, O_2, N_2, CH_4 and CO gases. Helium was the carrier gas and a thermal conductivity detector (TCD) was used. The CO_2 content was determined with a Chromosorb 102 packed column (1.83 m long × 3.175 mm outer diameter) with a mesh size of 80/100 and He as the carrier gas; a TCD was used. Once the composition of the gas was determined, its heating value and density were calculated, accordingly to the UNE-EN ISO 6976 standard, as a function of the mean gas composition and the heating value of each gas species.

2.3.2.2. Liquids.

There were two phases identified in the liquid fraction (heavy and light phases). The phases were separated by decantation. Both phases were considered for mass and energy balance. The heavy liquid phase was subjected to ultimate analysis and heating value determination as previously described in Section 2.3.1. The light phase was unable to ignite during its heating value determination, being considered as water for mass and energy balances.

2.4. Energy balance for the tests in the PPR

The energy input for a pyrolysis process is a key factor to determine the energy balance. This value depends on several parameters, such as pyrolysis temperature, energy losses, type of feedstock, and solids retention time. Thus, its value should be determined for each particular pyrolysis process, feedstock and pyrolysis conditions.

The mass balance was made by weighing the collected solid and liquid fractions at the end of the tests; the gas was calculated by difference. Therefore, the yields (wt.%) were obtained.

The energy input for this pyrolysis process is the product of the accumulated energy (in MJ) used in each test and includes the heat loss of the PPR, divided by the total amount of processed RVW (kg). Hence, the energy is referred to a kilogram of feedstock. The heat losses were determined with an empty run registering the energy used to keep the reactor at 550 °C for several hours.

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For the energy balance, the yield and energy content of each co-product were accounted. The energy contained in each co-product was calculated as shown in Eq. (1).

$$\text{Energy}_{a,b,c} = \eta_{a,b,c} \times \text{HHV}_{a,b,c} \tag{1}$$

where a,b,c, are pyrolysis co-products; η: co-products yield; HHV: co-products higher heating value.

The energy lost as heat in the co-products was calculated as shown in Eq. (2).

$$E_{\text{lost}} = \Sigma(m_{a,b,c} \times \text{Cp}_{a,b,c} \times \Delta T_{a,b,c}) \tag{2}$$

where *E:* energy; a,b,c,: are pyrolysis co-products; *m:* mass of the corresponding co-product; Cp: heat capacity of the corresponding co-product; ΔT: temperature change, from the exit temperature of each co-product to the reference temperature (25 °C).

2.5. *Potential carbon footprint reduction through a life cycle assessment (LCA)*

In order to calculate the potential reduction of carbon footprint in the winery industry by biochar production from the vineyard biomass and its application to soil, a LCA was performed. The LCA was done with the SimaPro v7.3.3 software (PRé Consultants, the Netherlands). The data were collected during the test runs of the MSPR and from the Ecoinvent v2.1 database. The emissions of CO_{2eq} were calculated with the impact assessment evaluation method: "Climate change 2001 IPCC GWP 100a" [29]. Three scenarios were analysed. (1) Biomass burning. (2) The MSPR works in stationary mode, the feedstock is transported to reactor and biochar to the application site. (3) The MSPR works in mobile mode, the reactor is transported to the vineyards and the biochar is applied in the vineyard where the reactor is. Thus, only the emissions of the reactor transport are considered. It is necessary to re-heat the pyrolyzer in each vineyard, so the propane gas consumption is raised. For scenarios 2 and 3, the biochar is mixed with compost in 1:1 proportion, so the same amount (in kg) of biochar produced is considered as avoided compost production. And the avoided emissions, from reducing compost production, are allocated to the biochar.

The CO_{2eq} for CO, CH_4 and N_2O emissions from the RVW burning were calculated (in a year basis) accordingly to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, being 42 336 tCO_{2eq}/yr. The CO_2 emissions were not considered because the new planted vines balance the removals and emissions in a 30–40 years period (the profitable exploitation lifespan of vines).

To evaluate the potential of carbon abatement of the biochar in soils, the long term stable carbon fraction in biochar was considered as 68% of the initial carbon content [30,31]. For the potential reduction of carbon footprint estimations, 21 vineyards and 7.1 million bottles per year (produced with grapes from these vineyards) of wine were considered.

3. Results and discussion

3.1. *Feedstock, ripped vines' wood (RVW) characterisation*

The results of the characterisation of the feedstock are given in Table 1. The RVW biomass has high ash content if compared to lignocellulosic biomasses used in other studies 0.5 to 10.8 wt.% [32–35]. The most similar biomass to the RVW is the land clearing wood, 16.6 wt.% (in dry basis) listed in Vassilev et al. [35]. This can be explained by the presence of soil residues that haven't been removed from both biomasses, and in the case of the RVW it is because the feedstock is intended to be used with minimal pretreatment. The values of the ultimate analysis (in a dry ash free basis), are in line with the lower limit values of C, O, H, N and S for wood biomass reported in Vassilev et al. [35].

Table 1
Charactersation of the RVW and charred solid products from PPR and MSPR.

	Feedstock (RVW)	RPP charred solid product	MSPR charred solid product
Moisture (wt.%)	9	1.59 (± 0.6)	1.75 (± 0.21)
Volatile matter[a] (wt.%)	70.79	20.96 (± 2.03)	13.5 (± 2.12)
Ash[a] (wt.%)	13.35	47.41 (± 1.85)	29.7 (± 1.13)
Fixed carbon[a,c] (wt.%)	15.86	31.63 (± 3.75)	56.8 (± 3.25)
C[b] (wt.%)	48.38	74.51 (± 5.28)	83.39 (± 6.32)
N[b] (wt.%)	0.4	0.66 (± 0.22)	0.73 (± 0.05)
H[b] (wt.%)	5.44	1.51 (± 0.24)	1.16 (± 0.09)
S[b] (wt.%)	0.1	0.05 (± 0.04)	0.09 (± 0.04)
O[b,c] (wt.%)	45.68	23.27 (± 5.39)	14.63 (± 6.32)
O/C	0.71	0.23	0.13
H/C	1.35	0.24	0.17
HHV (MJ/kg)	16.51	12.89 ± 1.84	21.38 ± 0.74

The numbers in the parentheses are the standard deviation (*n* = 3).

[a] In a dry matter basis.

[b] In a dry ash free basis.

[c] Calculated by difference.

3.2. *Pilot plant pyrolysis reactor tests*

The conducted tests on the PPR yielded useful information for the mass balance as well as for the energy balance. The characterization of the charred solid product is shown in Table 1. The C concentration in the charred solid product is higher than in the raw material, this is a consequence of the loss of volatile matter during the thermochemical conversion.The most abundant elements in the biomass are C, H and O. These three elements volatilize during pyrolysis process, but the H and O are lost in greater amounts than C, they are initially lost as water, and then as hydrocarbons, H_2, CO and CO_2 [4]. The low O content of the biochar is a consequence of the loss of functional groups (carbonyl and carboxyl) [36,37] during the process and it is more intense at higher pyrolysis temperatures [3,38]. Thus, higher pyrolysis temperature increases the fixed carbon amounts in the biochar and generally reduces the O content in the biochar [39].

The heating value of the charred solid products is generally higher than the raw material, but the high ash content (47.41 wt.%) of the charred product from the PPR decreased its energy content.

The results of the characterization of the gas fraction are given in Table 2. The gases generated during thermal degradation were mostly; CO, CO_2, light hydrocarbons (up to C_6 chains) and H_2. The formation of CO and CO_2 is a consequence of the decarboxylation processes [40]. The light hydrocarbons are the result of the cracking

Table 2
Composition and heating value of the gas co-product from the pyrolysis of RVW in the pilot plant reactor.

Gas species		% vol.
Methane	CH_4	14.07 (±1.2)
Ethylene	C_2H_4	2.42 (±0.31)
Ethane	C_2H_6	1.51 (±0.23)
Propylene	C_3H_6	1.13 (±0.21)
Propane	C_3H_8	0.2 (±0.04)
C_4–C_6 hydrocarbons	C_4H_{10};C_5H_{12};C_6H_{14}	0.06 (±0.02)
Hydrogen	H_2	9.53 (±1.52)
Carbon monoxide	CO	25.67 (±2.18)
Oxygen	O_2	0.55 (±0.2)
Carbon dioxide	CO_2	28.05 (±1.68)
Nitrogen	N_2	16.81 (±5.93)
Density (kg/m^3)		1.32
HHV (MJ/kg)		10.57
LHV (MJ/kg)		9.80

The numbers in the parentheses are the standard deviation (*n* = 3).

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Table 3
Key findings of the PPR tests including: yields, heating values, available energy and energy loses of co-products.

	Yield(wt.%)	HHV (MJ/kg)	Energy (MJ/$kg_{feedstock}$)	Exit temperature of co-products (°C)	Heat losses (MJ/$kg_{feestock}$)
Gas	43 (±3.25)	10.57	4.55	338	3.4
Liquids	17(±2.83)	5.71	0.97	70	0.34
-Heavy phase	20.5	27.85	5.71	70	4.40E-03
-Light phase	79.5	null	null	70	0.33
Char	40 (±3.11)	12.8	5.16	322	1.67

The numbers in the parentheses are the standard deviation ($n = 15$).

of heavier hydrocarbons having residence time long enough at high temperatures to react [37]. Meanwhile, the hydrogen in the raw material is released as H_2 at temperatures above 500 °C [41]. The gas species with more influence in the heating value were CH_4 and CO with 39% and 25% respectively, followed by ethylene with 8%. Despite having a low heating, the CO raises the heating value of the pyrolysis gas due its high proportion in it. Table 3 shows the co-product yields, their HHV values and available energy.

The energy balance was determined taking as a basis of calculation one kilogram of RVW. The energy input for the set of experiments was 2.79 ± 0.1 MJ/$kg_{feedstock}$ for this pyrolysis conditions.

Fig. 2 is a simplified Sankey diagram of the energy balance of the pyrolysis process for one kilogram of RVW. The energy balance would be zero if all the energy inputs and the energy outputs (available energy in co-products plus losses after the pyrolysis process) were equal; in this case this was not reached. There are 1.32 MJ/$kg_{feedstock}$ difference between input and output representing 6.86% of the energy input (energy stored within the feedstock and thermal energy). The mass balance was made by weighing the collected solid and liquid fractions; the gas was calculated by difference. So if accumulation of material occurred in the reactor, this could generate a measurement error affecting the mass balance and therefore the estimated energy available in each co-product. Based on previous experiences with the pilot plant, where energy balances ranged from 75.61 to 92.1% with a mean value of 82.1% ± 7.25 for a series of 4 different feedstocks, under the same pyrolysis conditions [38], the authors consider that energy balances around 90% are acceptable; in this case it was of 93.14% of the energy input.

3.3. Evaluation of the potential of self-sustainable pyrolysis process

The range of energy requirement for biomass pyrolysis varies depending on the type of feedstock, pyrolysis technology, conditions of the process (e.g., highest heating temperature and heating rate) among other factors. Crombie and Mašek [25] based on a literature review, adopted a range of energy of 6–15% biomass HHV required for pyrolysis. In the present work, the energy required by the PPR was determined as 2.79 MJ/$kg_{feedstock}$ or 16.9% of feedstock HHV which is higher than the previous statement. Nevertheless the conditions of the processes greatly affect the outcomes, by changing feedstock and pyrolysis temperature; the required energy input would change [38].

In order to assess the viability of a thermally self-sustainable pyrolysis process, the energy from gas and liquid co-products is considered via combustion. The solid fraction is the objective product, it is intended to be used as biochar, and thus its energy is not considered. The evaluation of the self-sustainable process is shown in Table 4.

The thermally self-sustainable pyrolysis process is achievable by gas and liquid combustion and still having a surplus energy that can be used in another process (e.g., for biomass drying).

Table 4
Evaluation of the self-sustainable viability of the pyrolysis process.

Energy demand (MJ/$kg_{feedstock}$)	Energy in gas and liquid co-products	Surplus energy	Self-sustainable?
2.79	5.52	2.73	Yes

3.4. Mobile and self-sustainable pyrolysis reactor (MSPR)

The design of the MSPR was done by Mecanotaf S.A. based on the data obtained during the tests in the PPR and the results of the characterisation of the co-products, mass and energy balances. The specifications to fulfil by the design were: able to treat 50–60 kg of feedstock per hour, utilise the gas and liquid co-products avoiding the condensation of the second one; be mobile and to work off-grid; able to reach and withstand pyrolysis temperatures of 500–800 °C; and to maximise environmental benefits of the biochar.

Once the reactor fabrication was finished, it was tested for biochar production performing several runs (commissioning). The main features are listed: treatment capacity, 50–60 kg/h of feedstock which was heterogeneous in particle size, ranging from fine material up to particles of 150 mm in length and up to approximately 50–75 mm in diameter.

The average temperatures of the combustion and the pyrolysis chambers were 754 ± 52 °C and 728 ± 53 °C respectively. The average temperature of the combustion gases at the outlet of the chimney was around 310 °C.

An average flow of material fed 55 kg/h was reached. The material flow might change depending on the type of material to be treated and its physical characteristics such as particle size and bulk density.

In the conditions described above the biochar yield was 26.67 wt.%.

3.5. Characterisation of charred solid product from the MSPR

The results of the characterisation of the biochar (charred solid product) from ripped vines' wood (BRVW) are presented in Table 1. The O/C and H/C molar ratios of the charred product offer information about the changes that the biomass underwent by the pyrolysis process. Biochar with H/C molar ratio about 0.3 have very highly condensed aromatic ring structure; and above 0.7 non-condensed aromatic structures such as lignin are present [42]. The biochar consists of multiple different forms of charred carbon in the black carbon continuum which comprises various substances like: graphite, soot, char and charcoal. The black C continuum also includes biomass and fossil fuels because the black carbon can be obtained by their combustion [39]. Determining the O/C molar ratio of a given charred material is useful to identify where in the black C continuum it may fit. The value of the O/C molar ratio that separates the thermo-chemical altered (pyrolysed) materials from biomass is 0.6, values above this correspond to those of biomass, and below it to biochar (or some form of black carbon) like mate-

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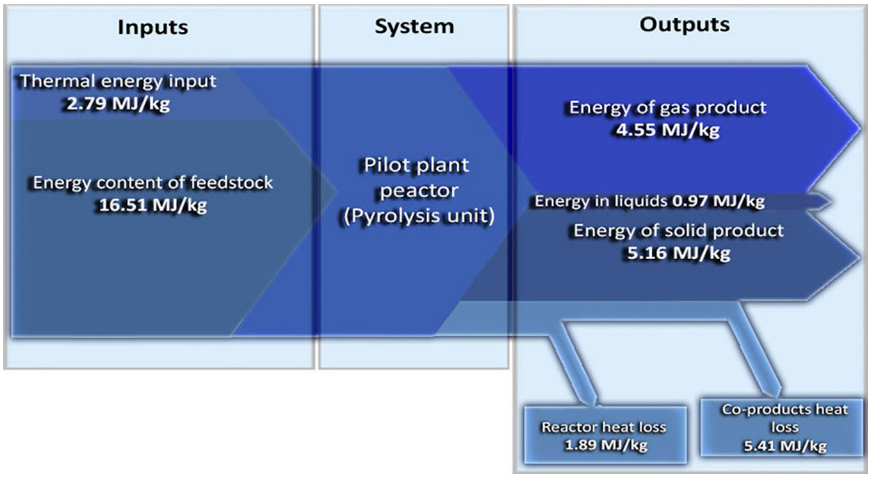

Fig. 2. Sankey diagram per kilogram of feedstock for the pyrolysis process in the PPR at 550 °C and 15 min of solid residence time.

Table 5
Results of the biochar characterised for soil amendment.

Parameter	Biochar from MSPR	Units
pH $(1:2,5)H_2O$	10	–
C.E. $(1:2,5)_{25}$	11.6	dS/m
Organic matter[a]	69.3	%
Organic carbon[a]	40.22	%
Total N[a]	0.48	%
Ammonia[a]	1.92	mg/kg
Nitric[a]	38.4	mg/kg
Organic N[a]	0.48	%
C/N	83.7	–
Phosphorus[a]	0.1	%
Calcium[a]	1.3	%
Magnesium[a]	0.4	%
Potassium[a]	2.3	%
Ca/Mg	3.3	–
K/Mg	5.8	–
Iron[a]	1135	mg/kg
Manganese[a]	108	mg/kg
Boron[a]	<0.1	mg/kg

[a] In a dry matter basis.

rials. The obtained biochar exhibit low H/C and O/C (0.17 and 0.13) molar ratios, which means it has higher stability [3,43] than the raw biomass enabling it to act as a carbon sink.

Comparing the characteristics of the charred solid products from the two pyrolysers (RPP and MSPR), there are some differences most likely due to the pyrolysis conditions in each reactor. The lower ash content in the MSPR charred solid product (29.7%) in comparison to the one from the RPP (47.41%) is a consequence of the feeding system used in the MSPR. The bucket elevator in the feeding system, apart from supplying the feedstock to the MSPR, it works as a sieve that preferably moves larger particles which generally carry lower soil residues. The fewer soil residues within the feedstock diminish the ash content in the charred solid product.

The higher pyrolysis temperature in the MSPR (728 °C), promotes the release of volatile matter to a greater extent than the mild pyrolysis temperature in the RPP (550 °C) having values of volatile matter content of 13.5 and 20.96% for MSPR and RPP respectively. The effect of high pyrolysis temperature is also evident in the variation of the H/C and O/C molar ratios. These molar ratios were low (high stability) for the charred solid product from the MSPR, thus, this charred solid product was selected over the one from the PRR to be studied for biochar applications.

The results of the characterisation of the biochar for soil amendment are shown in Table 5. The pH of the biochar should be considered as a determining factor for the type of soil that it may be applied to. Some indirect benefits on plants are attributed to the biochar capacity to maintain or raise the pH of the soil, such as, improve soil fertility, metal immobilization in contaminated soil, raise crops yield [44–48], but for some plants and microorganisms a change in soil's pH, especially in neutral and basic soils, may inhibit its activity [49] and nutrient availability for the plants. This biochar due to its high pH (10) might be recommended to be applied in acidic soils as neutraliser.

The supply of nutrients to soil by biochar application is not as straightforward as it might seem. The total nutrients in the biochar are not readily available to plants, since they are locked in the highly stable carbon structure of the biochar [49]. Nevertheless depending on the properties of the biochar, a fraction could be leached and utilised by soil biota [50]. Additionally, a series of benefits from biochar physical properties can be readily noticed in soil, such as: texture, structure, particle size distribution and density among others [51].

The C/N ratio in the biochar may seem to be problematic if applied to soil causing N immobilisation, values for C/N ratios of 25–35 in conventional soil amendments (such as compost) cause this effect [52]. Despite the high C/N ratio in biochar, its highly recalcitrant carbon structures [39] to microorganisms' activity in soil, it doesn't cause such N immobilization.

The concentration of heavy metals in the biochar and a verification of the categories that the biochar fulfils are shown in Table 6. The BRVW, comply with 4 out of 7 biochar categories proposed by the Spanish legislation for fertilizers [53]; the European Biochar Certificate (EBC) and the International Biochar Initiative (IBI) based on the content of heavy metals. The complying categories are class B and C in Spanish legislation on fertilizers and those limits of the IBI for International and European specifications.

The BRVW would not achieve basic or premium classification from the EBC because of the high Cu content for both classes and Ni for premium. Failing to get the class A designation in the Spanish legislation is also due to the slightly high Cu and Ni concentrations in the biochar.

3.6. *Potential carbon footprint reduction in wine production*

The data collected for the LCA (inventory) is presented in Table 7. This data was introduced in the SimaPro software and evaluated with the impact assessment evaluation method: "Climate change 2001 IPCC GWP 100a". The biomass burning does not have any effect on current carbon footprint of the process because it is the

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Table 6
Limits of admissible heavy metals (mg/kg in a dry basis), heavy metals concentration in the biochar from ripped vines' wood produced in the MSPR and standard categories it fulfils.

		Spanish legislation			EBC		IBI	
Element	Concentration in BRVW	Class A	Class B	Class C	Basic	Premium	International	European Union
Pb	10.2	45	150	200	150	120	70-500	121
Cd	<0.1	0.7	2	3	1.5	1	1.4-39	1.4
Cu	124	70 (nc)	300	400	100 (nc)	100 (nc)	63-1500	143
Ni	37.8	25 (nc)	90	100	50	30 (nc)	47-600	47
Hg	<0.1	0.4	1.5	2.5	1	1	1-17	1
Zn	100	200	500	1000	400	400	200-7000	416
Cr	69.3	70	250	300	90	80	64-1200	93

All metal contents are expressed in mg/kg in a dry basis.
nc: non-compliant.

Table 7
Data inventory for the life cycle assessment.

Description	Value (units)	Source
General LCA data		
Functional unit[*] (FU)	10.17 (t of wood)	
Bottles of wine (75 cl)	7.1 (million/year)	B. Torres
Vineyards	21	B. Torres
Total RVW	213.57 (t/year)	B. Torres
Compost production GHGs emissions	0.86 (kg CO_{2eq}/kg compost)	Ecoinvent database v2.1
MSPR operation related data		
Treatment capacity	55 (kg/h)	This work
Biochar yield	26.67 (wt.% dry basis)	This work
Propane gas consumption (17 to 790 °C)	19.65 (kg)	This work
Propane gas consumption (200 to 790 °C)	8.45 (kg)	This work
Diesel consumption, electric generator	0.63 (L/h)	This work
MSPR weight	13 (t)	This work
Transport related data		
Truck type for feedstock, biochar and MSPR transportation	EURO5; 7.5–16 (t)	Ecoinvent database v2.1
Average feedstock and biochar transportation distance (stationary pyrolizer)	66.1 (km)	This work
Average MSPR transportation distance(biomass and biochar not require transport)	30.2 (km)	This work
Ton-kilometers[**] (stationary pyrolyzer)	1882.88 (t km)	This work
Ton-kilometers[**] (MSPR)	392.3 (t km)	This work
Biochar from MSRP related data		
Biochar carbon content	64.14 (wt.% in a dry basis)	This work
Labile carbon content	15 (%C)	[31]
Stable carbon (<100 years)	17 (%C)	[31]
Highly stable carbon content (>100 years)	68 (%C)	[31]

[*] Amount of wood obtained from each of the 21 vineyards (in a dry basis).
[**] The transport process is expressed in ton-kilometers (t km), one ton-kilometer means the transport of one ton over 1 km.

current residue disposal. The results of the CO_{2eq} emissions for the pyrolyzer in stationary and mobile modes are presented in Table 8.

The CO_2 emissions from propane gas combustion in the mobile mode are higher (due to re-heating) comparing to the stationary one (see Table 8). Despite that, the total avoided CO_2 emissions from the mobile mode are higher than those from the stationary mode; this is a consequence of the reduced use of transportation, which is the most influential factor in the CO_2 accountability for this pyrolysis system.

The potential reduction of carbon footprint per bottle of wine found by the LCA was ≈17 gCO_{2eq}/bottle and ≈18 gCO_{2eq}/bottle for the MSPR in stationary and mobile mode respectively. The difference in CO_{2eq} emissions between the MSPR in stationary or mobile mode is 7.55 tCO_{2eq} yearly, this is equivalent to traveling 59 428 km or nearly 4.1 years traveling 40 km every day in an average european passenger car (127 gCO_2/km) [54]. Therefore, the utilization of the MSPR in mobile mode is a more effective strategy for climate change mitigation.

Table 8
Emission of CO_{2eq} of the MSPR in stationary and mobile modes.

Process	Stationary mode pyrolyzer	Mobile mode pyrolyzer
Diesel–electric generator (kg of CO_{2eq}/UF)	113	113
Propane gas for heating (kg of CO_{2eq}/UF)	80.4	121
Feedstock and biochar transport (kg of CO_{2eq}/UF)	505	105
Avoided compost production (kg of CO_{2eq}/UF)	−2340	−2340
Sequestred carbon (avoided kg of CO_{2eq}/UF by soil activity)	−3970	−3970
Total (kg of CO_{2eq}/UF)	−5611.6	−5971
Avoided tones of CO_{2eq} emissions yearly	−117.84	−125.39
Avoided grams of CO_{2eq}/bottle of wine emissions yearly	−16.6	−17.66

Negative sign means avoided emissions.

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4. Conclusions

The production of biochar from vineyard residues in a self-sustainable pyrolysis process is possible; this was confirmed by the biochar production in the mobile and self-sustainable demonstration pyrolyzer. Furthermore, it is feasible to produce biochar at the biomass source and with little pre-treatment. Using a mobile reactor, the transportation of feedstock is nearly non-existent, thus reducing CO_2 emissions associated to transport and external energy demand. The produced biochar fulfils the criteria of heavy metals content for fertiliser class B and C of the Spanish legislation, and is below those limits given by the International Biochar Initiative for the European Union. More experimentation will be needed to produce biochar complying with all the heavy metals (with special attention to Cu and Ni content) limits set by the EBC and to get a better classification in the Spanish legislation. The biochar form ripped vines wood exhibits low H/C and O/C molar ratios (0.17 and 0.13 respectively) suggesting highly stable carbon structures making it suitable for carbon storage. Producing biochar in the self-sustainable pyrolysis reactor and applying it to the soil instead of burning the biomass leads to significant carbon footprint reductions in the winery industry, enhancing the social and environmental responsibility of this economic sector.

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